



Hydrolytically synthesized chlorinated bioactive glasses: Structural reticulation and controlled ion release without alkaline shift

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ABSTRACT

Bioactive glasses are recognized for their ability to release ions and induce apatite formation in physiological media. However, conventional glasses often cause a marked increase in pH during dissolution, which may lead to cytotoxic effects. In this study, chlorinated bioactive glasses were synthesized via a hydrolytic sol-gel route using tetraethyl orthosilicate (TEOS) and calcium chloride, aiming to obtain materials with efficient ionic release and controlled pH response. Samples were thermally treated at 500 °C, 600 °C, and 700 °C and characterized by FTIR, Raman spectroscopy, specific surface area (BET), scanning electron microscopy (SEM), and ionic release tests. The chlorinated bioactive glass calcined at 500 °C exhibited the most promising combination of characteristics: presence of hydroxyl groups (-OH), a structure predominantly composed of Q² units, high specific surface area (31.75 m² g⁻¹), well-defined mesoporosity, high ionic release (~2000 μS cm⁻¹), and effective control of pH increase in aqueous media. These properties directly contribute to bioactivity and indicate that this material can be incorporated into biomedical formulations without the need for prior neutralization steps, in contrast to many conventional bioactive glasses. The results also demonstrate that the hydrolytic sol-gel route enables the synthesis of chlorinated bioactive glasses with tunable structure and dissolution profiles, overcoming limitations associated with more complex routes, such as those based on ion-exchange resins or precursors like metasilicate. The ability to combine high ionic release with low impact on pH represents a relevant advance in the design of bioceramics for regenerative and dental applications.

1. Introduction

The progressive aging of the global population and the increase in life expectancy have intensified the demand for biomaterials aimed at the regeneration of mineralized tissues, such as bone and dentin. Among the various candidates, bioactive glasses stand out due to their ability to release bioactive ions, promote hydroxyapatite formation, and stimulate favorable cellular responses, making them widely used in dental and orthopedic applications [1,2].

Since their introduction by Larry Hench in the 1970s with the development of the 45S5 bioactive glass via melt-quenching [3–10], these materials have evolved considerably. However, the melt-derived route presents several limitations, such as high processing temperatures, compositional heterogeneity, and restrictions in incorporating

volatile elements [3,9–14]. As an alternative, sol-gel synthesis routes have gained attention for enabling improved compositional control and higher specific surface area, which enhances bioactivity [9–12,15–21]. Nevertheless, reproducing the 45S5 composition via sol-gel remains challenging due to thermal decomposition of nitrate precursors and low thermal stability, which leads to premature crystallization during calcination [12,13,16].

To overcome this, the sodium-free 58S composition was proposed, which presents higher crystallization temperatures and avoids early devitrification [9,12,13,16]. Still, these materials tend to raise the pH significantly when in contact with aqueous media due to hydroxide formation during dissolution, a phenomenon that becomes critical when working with fine powders [3,13,15,16,22,23]. This pH elevation can reach cytotoxic levels, leading to protein denaturation and

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